A Study of the Steric Requirements of the 9-Anthracyl Group and Their Contribution to the Preparation of 9-Anthracylboron Compounds

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A STUDY OF THE STERIC REQUIREMENTS OF THE 9-ANTHRACYL GROUP AND THEIR CONTRIBUTION TO THE PREPARATION OF 9-ANTHRACYLBORON COMPOUNDS

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The differences in the chemical behavior of certain trialkylboranes have been attributed to the steric requirements of the alkyl groups in the boron derivative (Brown, 1945). These irregularities are even more conspicuous when three large bulky aryl groups are attached to the boron atom. For example, the chemical activity of triphenylborane, tri-a-naphthylborane,2 and trimesitylborane2 has been found to decrease in that order (Brown and Dodson, 1957).

It was of interest to prepare tri-9-anthracylborane3 and to compare its reactivity with that of TNB and TMB. An examination of the space models of the three triarylboranes shows that the boron atom is shielded by the surrounding aryl groups in the order TNB < TAB < TMB. Since most of the reactions of triarylboranes involve an attack on the boron-carbon bond, the chemical activity of the three compounds should be of the opposite order. Simplified line drawings of the three triarylboranes are shown in figure 1.

EXPERIMENTAL PROCEDURE

Since several triarylboranes have been prepared by the reaction of the aryl Grignard reagent with boron trifluoride, it seemed probable that this method could be applied to the synthesis of TAB. Commercial boron trifluoride-etherate, made by Eastman Kodak Co., was distilled in an all glass apparatus at reduced pressure and in an atmosphere of dry nitrogen. The water white portion boiling over the range 75 to 76°C at 73 mm Hg pressure was collected and stored in a glass stoppered receiver.

The method of Barnett and Cook (Shirley, 1951) was used to prepare 9-bromoanthracene. Anthracene was first converted to 9,10-dibromo-9,10-dihydroanthracene. This was dehydrohalogenated to form the desired 9-bromo derivative. The product melted over the range 99 to 100°C3 after successive recrystallizations from ethanol and ligroin (b.p. 100 to 110°C).

The 9-anthracylmagnesium bromide Grignard reagent was prepared by reacting 9-bromoanthracene with purified magnesium in anhydrous diethyl ether. Five drops of ethyl bromide were added to initiate the reaction. The preparations were carried out in an all glass apparatus which consisted of a three neck flask fitted with a mechanical stirrer, reflux condenser, and a dropping funnel. Dry nitrogen gas was passed through the apparatus during the preparations.

In a typical preparation a solution of 5.1 gm of 9-bromoanthracene (0.02 moles) in 50 ml of anhydrous ether was added slowly from the dropping funnel to a mixture of 1.0 gm of magnesium (0.04 moles), 50 ml of anhydrous ether and five drops of ethyl bromide in the three neck flask. The mixture was continuously refluxed during the addition, which required approximately one hour, and for 23 hours after the addition was complete. At the end of the twenty-four hour reaction period a small quantity of the mixture was withdrawn from the flask and the amount of Grignard reagent present was determined (Gilman et al., 1923).
In all of the preparations reported here the amount of 9-anthracyl magnesium bromide formed was in the range of 60 to 65 percent of the theoretical quantity.

In attempting to prepare TAB, freshly distilled boron trifluoride-etherate was dissolved in anhydrous diethyl ether and added slowly to the Grignard reagent in the flask in which the later had been formed. The reaction mixture was continuously stirred and refluxed during the addition and for various periods of time after the addition was complete. Dry nitrogen gas was passed through the system during the addition and subsequent refluxing. In several trial runs dry toluene was added to the Grignard reagent prior to the addition of the boron trifluoride-etherate and the ether was removed by distillation. This allowed the use of a higher reflux temperature during the preparation. The mole ratios of boron trifluoride-etherate to 9-anthracylmagnesium bromide used varied from 1:1.8 to 1:8 and the duration of reflux after addition was complete varied from 2 to 120 hours.

After the refluxing period the entire mixture was added to 100 ml of cold water. When the initial reaction had subsided, 10 ml of concentrated hydrochloric acid was added slowly with stirring and shaking. The organic layer was removed, washed with four 100 ml portions of water, dried over anhydrous calcium chloride, and concentrated by distillation until slightly cloudy. The mixture was cooled in an ice bath and the precipitated solid was removed by filtration. The solid was yellow in color and identified as anthracene from its melting point (213 to 216°C) and that of its picrate derivative (137 to 139°C). The filtrate was evaporated to dryness and the residue was twice recrystallized from ligroin (b.p. 100 to 110°C). The bright orange solid product melted at 152.5°C and contained 2.80 percent boron, 85.80 percent carbon, and 5.05 percent hydrogen. The method used in the boron analysis has been previously described (Fowler and Kraus, 1940). These values were in good agreement with those calculated for di-9-anthracylborinic acid, \((C_{14}H_{9})_2\text{BOH}\) (2.83 percent boron, 87.97 percent carbon, and 5.01 percent hydrogen). The deviations between the measured and calculated percent composition were attributed to a small amount of occluded ligroin in the sample. Di-9-anthracylborinic acid is very soluble in benzene, ether, chloroform and toluene, moderately soluble in ligroin, and slightly soluble in ethanol.
The reaction between boron trifluoride-etherate and 9-anthracylmagnesium bromide in mole ratios varying from 1:3.4 to 1:8 gave the same product, the diarylborinic acid. Refluxing the mixtures in toluene for periods up to 124 hours only improved the yield but did not produce TAB as originally predicted. No attempt was made to isolate and characterize the intermediate, di-9-anthracylboron fluoride.

Several triarylboron compounds have been purified by vacuum sublimation (Chu and Weismann, 1956a, b). A portion of di-9-anthracylborinic acid was subjected to such a treatment in an effort to simplify its purification. The bath surrounding the sublimation apparatus was maintained at temperatures between 115 and 120°C for a period of three hours. A yellow sublimate was identified as anthracene from its melting point. The sublimand was orange brown in color and melted at 145°C to a viscous dark brown liquid. A boron analysis of the material indicated that it was 9-anthracylboric oxide, C_{14}H_{9}BO (found, 5.32 percent boron; calculated, 5.30 percent boron). The reaction was pictured as follows:

\[
\begin{align*}
\text{120°C} & \quad (C_{14}H_{9}O)_{2}BOH \underset{\text{reduced pressure}}{\xrightarrow{\text{\textbullet}}} C_{14}H_{20}+C_{14}H_{9}BO \\
\end{align*}
\]

When di-9-anthracylborinic acid was heated in air at 225°C slow decomposition occurred, leading to the formation of anthraquinone and 9-anthracylboric oxide. The former was identified from its melting point (283 to 286°C) and that of its oxime derivative (221 to 223°C).

\[
\begin{align*}
\text{225°C} & \quad (C_{14}H_{9})_{2}BOH+3/2 \text{O}_{2} \xrightarrow{\text{}} C_{14}H_{8}O_{2}+C_{14}H_{9}BO+\text{H}_{2}\text{O} \\
\end{align*}
\]

The stability of di-9-anthracylborinic acid in hot dilute hydrochloric acid, hot dilute sodium hydroxide, and in hot water was investigated by refluxing portions of the acid in each of these reagents. The first two reagents produced anthracene and substances that melted at 180 to 184°C and 209 to 213°C, respectively. The first of these was identified as 9-anthracylboronic acid, C_{14}H_{9}B(OH)_{2}, from its boron content (found, 4.82 percent boron; calculated, 4.88 percent boron). The second compound was identified as the disodium salt of 9-anthracylboronic acid, C_{14}H_{9}B(ONa)_{2} (found, 3.70 percent boron; calculated, 3.76 percent boron). Boiling water caused no appreciable change in the original material.

DISCUSSION

A comparison of the Fisher-Hirschfelder models of TNB, TAB, and TMB indicates that the degree of crowding around the central boron atom increases in that order. TNB is fairly easy to prepare and the yields are good (Brown and Sujishi, 1948). TMB can be prepared in fair yields with some difficulty (Brown and Dodson, 1957). It seems reasonable to assume that if steric requirements of the aryl groups are the major factor in the preparation, TAB could be prepared using conditions approximating those employed in the synthesis of TMB. Such is not the case. Even when conditions more strenuous than those employed in the preparation of TMB are used, only the disubstituted aryl boron compound is formed.

The reactions of the arylborinic acids reported here and in the literature also points to an increase in the steric requirements of the aryl groups as one goes from a-naphthyl to the 9-anthracyl and finally to the mesityl group. The chemical behavior of di-9-anthracylborinic acid is very similar to that of di-a-naphthylborinic acid (Brown and Dodson, 1957). This would indicate that the steric influence of the two aryl groups, a-naphthyl and 9-anthracyl, are approximately the same. Since the chemical activity of dimesitylborinic acid is considerably less than that
of either, it must be concluded that the steric influence of the mesityl group is greater than that of either the a-naphthyl or the 9-anthracyl group.

The repulsion forces of the pi electrons in the anthracyl group, especially those in the vicinity of the 1 and 8 carbon atoms, might account for the reluctance of TAB to form. The models reveal that the 1 and 8 carbon atoms in the trisubstituted boron compound are very close to each other. Overlapping of pi electronic fields would lead to considerable repulsion between neighboring 9-anthracyl groups. In di-9-anthracylboron compounds, such as the fluoride or borinic acid, the two 9-anthracyl groups can rotate to a certain extent about the carbon-boron bond and the 1 and 8 carbon atoms of the two groups exhibit no overlapping. In TNB the possible repulsion of the pi electrons at the number 7 carbon atoms in the aryl groups is avoided because the three groups can rotate about the carbon-boron bond to such an extent that the number 7 carbon atoms do not overlap. Furthermore, there is evidence that TNB exists in both the symmetrical and unsymmetrical forms (Brown and Sujishi, 1948). In the latter form the number 7 carbon atoms in the three aryl groups are considerably far apart.

LITERATURE CITED


